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Kyoto University

THE SAKURADA LABORATORY

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Studies in Synthetic Fiber Vinylon

Some historical remarks

Since the foundation of this institute researches were carried out in the Kita Laboratory on viscose and acetate rayon. A study in pure synthetic fiber was begun in the spring of 1938, and it has been continued in the Sakurada Laboratory.

At the beginning of this research wet- and dry-spinning of well known synthetic resins i. e. polyvinyl acetate, polymethyl methacrylate and polystyrene was studied.[1),2)] Being stimulated by the pulication of nylon in the U. S. the scale of the research was enlarged. Polyvinyl alcohol was selected as the starting material, while research had been already carried out in this laboratory on the saponification of polyvinyl acetate as a basic study of the mechanism of high polymer reaction.[3)] At first it was intended to obtain polyvinyl amine through the amination of *p*-toluene sulfonic acid ester of polyvinyl alcohol. As this was not fruitful, so experiments were begun to prepare synthetic fibers from polyvinyl alcohol itself. The results of the experiments were made public in 1939, and the new fiber was called "Gosei-ichigo" i.e. "Synthesis I"[4)]. A little later Kanegafuchi Spinning Co. Ltd. announced "Kanebiyan". "Gosei-ichigo" and "Kanebiyan" were results of independent research, but manufacturing methods and properties of the two fibers were similar.

An idea to produce synthetic fiber from polyvinyl alcohol is not new. Various attempts are to be seen in the patent literauture, but none has succeeded to produce textile fiber of practical value. The success of the experiments in this laboratory is based upon the combined method of heat treatment of water soluble polyvinyl alcohol fiber and formalization. The fiber is no more soluble in boiling water, and neither remarkable shrinkage nor softening occurs in it. Resistance to dry heat is as high as acetate rayon and nylon.

Under the auspicies of "Gosei-senni Kenkyu Kyokai (Society of Synthetic Fibers)" a pilot plant and a laboratory were founded in this institute in 1941. Hence various researches for the industrial production of this new fiber have been carried out, and foundation for its industrialization was established.

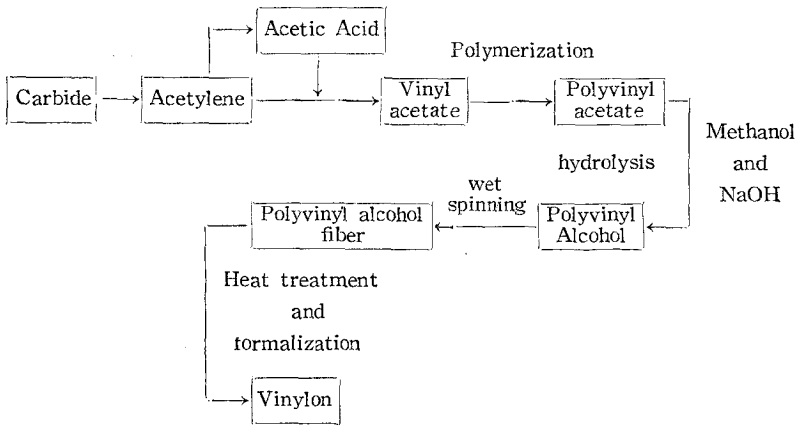
Though World War II prevented an early idustrialization of this new fiber, the following four plants have already started for the commercial production of this new fiber: Kurashiki and Okayama plant of Kurashiki Rayon Co. Ltd., Sagoshi plant of Dai-Nippon Spinning Co. Ltd. and Ogaki plant of Nihon Synthetic Fiber Co. Ltd. Besides the above four plants, which have adopted the process of the dry heat treatment according to the results of the basic studies of this institute, the Yodogawa plant of Kanegafuchi Spinning Co. Ltd. is also now in operation.

"Vinylon" is a generic name given under a general consent by the Japanese

scientists and engineers concerned in May, 1948, to the synthetic fibers made from polyvinyl alcohol.

Manufacture of Vinylon

An orientation flow sheet of manufacture of vinylon is given below:

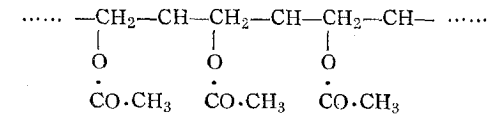


a. Polymerization of vinylacetate

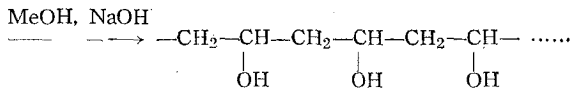
Vinyl acetate is polymerized either by an emulsion[5] or solution process. Newly developed suspension polymerization is also fitted for this purpose. The degree of polymerization of polyvinyl acetate must be so high that it gives polyvinyl alcohol, whose degree of polymerization lies between 1000 and 1500.[7]

b. Manufacture of polyvinyl alcohol

Polyvinyl alcohol is obtained by the catalytic hydrolysis of polyvinyl acetate. It is reacted with methanol in the presence of a small ammount of caustic soda as a hydrolysis catalyst.[8]



Polyvinyl acetate



Polyvinyl alcohol

The true mechanism of reaction is not hydrolysis but ester interchange between polyvinyl acetate and methanol.[9]

Degree of hydrolysis should be higher than 99% and ash content less than 0.5%, while residual acetyl groups have a negative effect on the heat treatment, and ash (sodium acetate) accelerates discoloration at higher temperature.[10]

c. Preparation of spinning solution

When it is necessary, polyvinyl alcohol powder is washed with cold water to lower the ash content, and then dissolved in hot water. The concentration of the solution is about 15%. Occasionally a small quantity of sodium and zinc sulfate is added to the solution to facilitate the coagulation by spinning.

d. Spinning

Spinning of polyvinyl alcohol is essentially same as the viscose process.[11] It is not necessary to ripen the solution for spinning. The coagulation bath contains no acid, and during the spinning no toxic gas is evolved. Coagulation occurs not through chemical reaction but through colloid chemical one i. e. dehydration.[12] Typical examples of spinning solution, composition of the coagulation bath and conditions of spinning are given below.[13]

Examples of spinning solution:

		Example I	Exmple II
Polyvinyl alcohol	%	14.0	16.0
Salt*	%	2.0	1.0
Water	%	84.0	83.0
Viscosity**	seconds	20	40

* $Na_2SO_4+ZnSO_4$ (the composition is same as that of the coagulation bath).
** Time required for a steel ball of 1/8″ diameter to fall a 20cm column of the solution at 30°C.

Composition of the coagulation bath:

Na_2SO_4 380–400 g/l, $ZnSO_4$ 20–30 g/l.

Conditions of spinning:

Temperature of spinning solution ..... ca 70°C.
Bath temperature ..... 45°C.
Bath length (dip length)..... 50–200 cm (ordinary 100 cm).
Rate of spinning ..... 50 m/min.

Fresh fibers are soluble in cold water, but after sharp drying they are no more soluble. To obtain fibers insoluble in boiling water, they must be subjected to the heat treatment and formalization.

e. Stretching

Vinylon fibers, like many other synthetic fibers, attain high degrees of molecular orientation as a result of stretching under suitable conditions. The highest tenacity attained by laboratory scale experiments is 8 g/den. with elongation of 12%. Vinylon can be stretched at various stages.

a. Stretching of wet fibers during or immediately after spinning at a lower temperature.[14]
b. Stretching after drying at an elevated temperature (usually at about 180°C).[15]
c. Stretching during heat treatment.[16]
d. Stretching after heat treatment.[17]

In commercial operations method a or b is ordinary adopted.

f. Heat treatment

This is the most important technique in the manufacture of venylon.[18] After stretching, the fibers which contain yet a large ammount of salt from coagulation bath, are subjected to the heat treatment. The process is carried out either under or without tension in a hot air atomosphere at temperatures ranging from 210 to 220°C. The time required for this process is from 5 to 10 min. for tow and 1 minute for filament yarn. The heat treatment alone has a big effect on fiber properties.[19] In comparison to dried fibers which shrink in water at 30°C to one half of their initial length and show rubber like elasticity, the shrinkage temperature of fibers after the proper heat treatment is above 85°C. Effect of heat treatment is further given in Table 1.

Table 1. Effect of the heat treatment after the subsequent formalization of fibers.

Temp. of heat-treatment °C	Schrinkage of fibers in water at various temperaturs in %						Temp. of shrinkage of dry fiber. °C*
	45°C	55°C	65°C	75°C	86°C	95°C	
130	1.47	9.23	34.4	61.4	64.2	70.5	158
145	1.89	5.94	22.9	51.7	65.1	69.7	163
160	0.45	1.34	6.69	24.6	50.4	61.1	177
170	0.0	0.0	4.18	12.2	45.8	63.3	181
180	0.0	0.0	2.31	5.5	36.2	65.9	197
190	0.0	0.0	0.90	2.3	7.7	50.1	202
200	0.0	0.0	0.99	1.98	3.43	8.82	196
210	0.0	0.0	0.92	0.44	1.40	2.23	209

* Temp. of the air atomosphere at which the fiber shrinks to 2/3 of their initial length.

When the heat treatment is carried out under no tension, crimped vinylon is obtained.[13] The stability of the crimp is not especially high. By the vertical heat treatment the fibers own weight disturbs the spontaneous crimping of the fibers.

Kanegafuchi Spinning Co. Ltd. suggested a wet heat treatment in the 48-50% solution of ammonium sulfate at 140°C (30-40 pounds pressure). The treatment requires from 1 to 2 hrs. The effect of this wet heat treatment is somewhat less than the dry heat treatment at 215°C.

To avoid discoloration in the dry heat treatment it is necessary that either P. H. of the coagulation bath is maintained at about 2 or a small amount of $MgSO_4$ or $ZnSO_4$ is added to the bath.[20] By ordinary operations the latter method is preferable, and $ZnSO_4$ is added to the bath.

An X-ray analysis shows that the heat treatment brings about not only an increase in the degree of crystallinity but also spacings of crystal lattices is shortened to a certain degree.[21]

Table 2. Change of spacings of polyvinyl alcohol crystal through heat treatment.

Interference \ Sample	P.V.A. fiber Befor heat treat.	P.V.A. fiber After heat treat.
A_1	8.21Å	7.64
A_4	4.60	4.54
A_5	v. weak	3.84
A_5	—	4.13
A_3	—	2.77
I_0	2.45	2.45
I_1	2.22	2.22

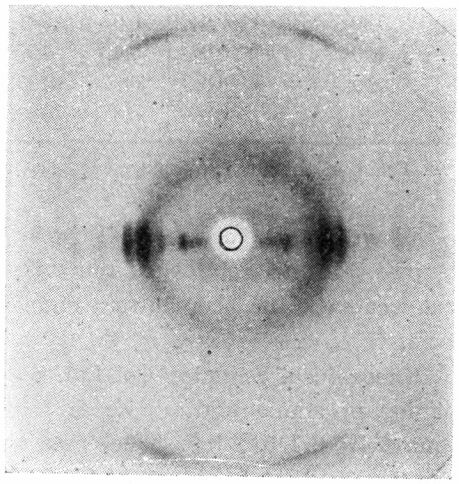
g. Formalization

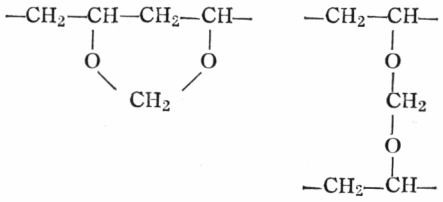
The formalization of fibers is carried out at a temperature between 75 and 80°C during 40 min. An example of the formalization bath is as follows:[13]

H_2SO_4 20%, Na_2SO_4 25%, HCHO 4%, H_2O 51%

Na_2SO_4 is added to prevent softening of fiber by formalization. The reaction must be so conducted that only the amorphous part is formalized. The suitable degree of formalization lies between 35 and 45% of the total OH groups of polyvinyl alcohol. As is shown in Fig. 1, X-ray diagramm of vinylon is that of unchanged polyvinyl alcohol.[22] It seems that not only itramolecular but also intermolecular formalization takes place with this reaction.

Fig. 1. X-ray diagram of Vinylon.





Fibers are washed after formalization with water, then oiled, cutted and dried.

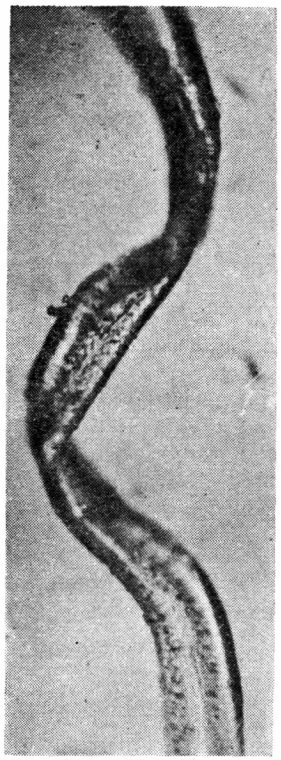
Until today research was concentrated for the production of staple fiber, but continuous filament yarn can also be produced in the same way. In the latter case it is necessary that eveness of the heat treatment and formalization is improved.

Properties of Vinylon

The microscopic longitudinal and cross-sectional views of vinylon are given in Fig. 2. The cross sections have a kidney-like appearance, and the fibers have a dense skin with rather porous, spongy case.[23]

Fig. 2. Microscopic longitudinal and cross-sectional view of Vinylon.

Crimped Vinylon. Ordinary Vinylon.



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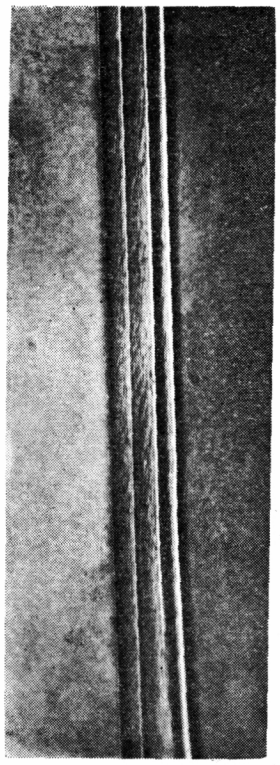

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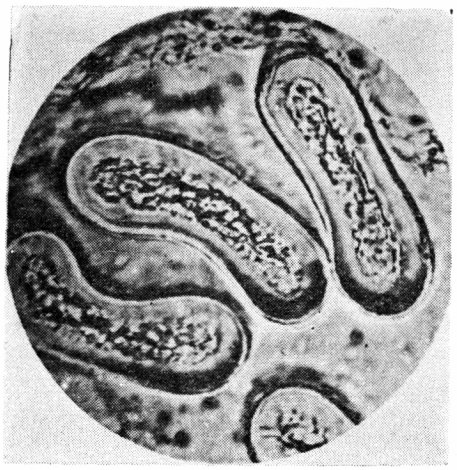

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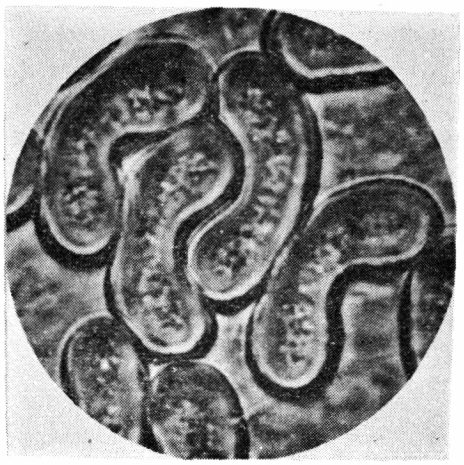

d

General properties[24] of vinylon fibere are given in Table 3.

Table 3. General properties of vinylon.

Tensile strength (g.p.d.)	Std. 2-6
	Wet About 70% of std.
Elongation (%)	Std. 15-30
	Wet From 10 to 20% greater than that of std.
Elastic recovery (%)	98% at 2%, 80% at 4%
Specific gravity	1.30
Regain (65% r. h.)	2-3%
Effect of heat	Effect on strength of 20°C
	91% at 50°C, 66% at 100°C
	37% at 150°C, 13% at 200°C
Effect of hot water	Effect on wet strength of 20°C
	67% at 50°C, 50% at 75°C
	30% at 95°C
Effect of age	None
Effect of sunlight	Loses strength on prolonged exposure.
Effect of acids	Better than viscose rayon and cotton.
	No loss of strength after 10 hrs immersion in 10% HCl at. 50°C.
Effect of alkalis	No effect
Effect of other chemicals	Strong oxidising agents degradates slowly.
Effect of organic solvents	Not harmed by common solvents.
Dyes used	Acetate, naphthole, basic, substantive
Resistance to moth	Wholly
Resistance to mildew	Believed to be wholly
Stretch resistance	2% elongation 0.3 g.p.d.
	10% 〃 3 g.p.d.
Abraison resistance (fiber)	50.000 cycles
	(wool 970, silk 4900, viscose rayon 650, nylon 10.000)

Dyeing

Vinylon can be dyed with acetate, naphthole, sulphur and vat colors.[25] Some basic and direct cotton dyes may also be used. Shade is generally not deep.

Bleaching. Although vinylon can be bleached with calcium hypochlorite solution without serious loss of tenacity, sodium chlorite is more suitable for this purpose.

One of the outstanding properties of vinylon is its high resistance to abraision. It is true that vinylon is thermoplastic, however, shrinking temperature is higher than 200°C when it is dry, and about 110°C when wet.[19] Unlike other vinyl fibers, vinylon is permeable to water. Vinylon may be regarded as an all purpose fiber, whose properties are intermediate between the properties of ordinary vinyl fibers and those of rayon.

Studies in the improvement of vinylon is being continued in this laboratory. Vinylon AN is an example of it.[26] When heat treated, polyvinyl alcohol fiber is acetalyzed with chloracetaldehyde instead of formaldehyde, and subsequently aminated with ammonia or amines such as ethylene diamine, and thus vinylon AN is obtained. Affinity for dyes of this new type of vinylon is similar to wool, and resistance to hot water is about 20°C higher than ordinary vinylon. Like cellulose fiber vinylon has many potentialities of further chemical improvement.

We wish to express our sincere thanks to Professor G. Kita for his guidance and help during the course of the above-mentioned study. We are also indebted to Nihon Kagaku Sen-i Kenkyusho (Nihon Institute for Chemical Fibers) and Kobunshi Kagakn Kyokai (Society of Chemistry of High Polymers, previously Society of Synthetic Fibers) for financial assistance through which this investigation and development work could be accomplished.

1) G. Kita: Annual Rep. Inst. Chem. Fibers, **3**, 7 (1938).
2) I. Tsukahara: *Ibid.* **4**, 41 (1939)
3) I. Sakurada and S. Lee: Z. physik. Chem. A **184**, 268 (1939).
4) S. Lee: Annual Rep. Inst. Chem. Fibers, 1939, **4**, 51 (1939).
5) S. Okamura: Preparation and Application of Vinyl Resin Emulsion. 1947, Kyoto, Japan.
6) R. Inoue and I. Sakurada: Chem. High Polymers, Japan, **7**, 211 (1950).
7) I. Sakurada and K. Fujikawa: Chem. High Polymers, Japan, **2**, 143 A. Nakajima: *Ibid.* **7**, **57**, (1950).
8) S. Michitaka: Annual Rep. Inst. Chem. Fibers, **6**, 203 (1941).
9) I. Sakurada and T. Osugi: Studies on synthetic fibers, **2**, 192. (1944).
10) unpublished
11) H. Kawakami: Annual Rep. Inst. Chem. Fibers, **6**, 217 (1941); S. Lee, H. Kawakami and K. Yoshimasu, J. Soc. Chem. Ind. Japan, **44**, 227 (1941).
12) E. Nagai: Annual Rep. Inst. Chem. Fibers, **5**, 5 (1940).
13) S. Lee: Annual Rep. Inst. Chem. Fibers, 8, 219 (1942); H. Kawakami: *ibid*, 167; S. Lee: Chem. High Polymers, Japan, **2**, 175 (1945).
14) H. Kawakami, S. *Lee*: Chem. High Polymers, Japan, **3**, 6, 13, (1946).
15) S. Lee and K. Hitomi, Chem. High Polymers, Japan **2**, 1. (1940).
16) unpublished.
17) unpublished.
18) S. Lee, H. Kawakami and K. Hitomi: Annual Rep. Inst. Chem. Fibers, **5**, 115, (1940)
19) W. Tsuji: Annual Rep. Inst. Chem. Fibers, **6**, 255, (1941).
20) H. Kwakami: Annual Rep. Inst. Chem. Fibers, **6**, 221 (1941).
21) K. Fuchino: Annual Rep. Inst. Chem. Fibers, 1941, **6**, 267, (1941); I. Sakurada and K. Fuchino: Bl. Inst. Phys. and Chem. Res. **21**, 1077, (1942).
22) I. Sakurada and K. Fuchino: Bl. Inst. Phys. and Chem. Res. **20**, 898, (1941).
23) K. Hirabayashi: Annual Rep. Inst. Chem. Fibers, **4**, 11, (1939); Studies on synthetic fibers, **1**, **68**, (1943).
24) S. Lee: Annual Rep. Inst. Chem. Fibers, **6**, 271, (1941).
25) H. Yoshitake: Dyeing of Vinylon, Kyoto 1951.
26) unpublished.